



Gasification of oil palm residues (empty fruit bunch) in an entrained-flow gasifier

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ABSTRACT

Empty fruit bunch (EFB) biomass, one of the most abundant biomass residues in Southeast Asia, was gasified using H₂O (steam) or H₂O + O₂ as a gasification agent in an entrained-flow gasifier at 900 °C. During gasification with H₂O alone, the EFB gasification rate was >95% (C-equivalent), and hydrogen-rich gas with a composition suitable for liquid fuel synthesis ([H₂]/[CO] ≈ 1.8–3.9, depending on the [H₂O]/[C] ratio) was obtained. The gasification rate improved (to >99%) when O₂ was added to H₂O; however, under these conditions, the gas composition was less suitable for liquid fuel synthesis (the amount of [CO₂] increased, the amounts of [CO] and [H₂] decreased, and the [H₂]/[CO] ratio decreased). Nevertheless, the [H₂]/[CO] ratio was sufficient (~2) for liquid fuel synthesis. We also performed thermogravimetric (TG) analysis of EFB using a thermobalance specially designed for analysis of feedstock in the presence of O₂, H₂O, or both. TG analysis suggested that EFB decomposed easily, especially in the presence of H₂O and/or O₂. The results obtained from TG analysis and gasification agreed well. In gasification, the tar yield was low (<0.1 wt.%), and the tar was composed mainly of six compounds, including naphthalene; these results suggest that the primary tar decomposed and that gasification proceeded quite well. The yield of solid residues was low, and the soft, yellow residues, which partially adhered to the gasifier wall, were composed mainly of ash. These solid residues would require treatment in a large-scale gasifier.

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1. Introduction

In 2002, biomass was first approved as a renewable source of energy by the Japanese government, and targets for the introduction of biomass were set. The target values were revised in 2006, at which time bio-fuel (also referred to as liquid bio-fuel), which is fermented or synthesized from biomass and used for vehicles, was first nominated. According to the government scenario, more than 0.5 million kl of bio-fuel will be introduced every year up to 2010, and the yearly amount will gradually be increased until 2030 [1]. Although bioethanol is the main gasoline substitute in use at the moment, biodiesel fuel will also be introduced after 2020. Among them, second-generation bio-fuels, such as liquid fuel synthesized catalytically from gasified biomass, are expected (and required) to become the main substitutes for petroleum diesel fuel.

The production of bioethanol by fermentation of food biomass, such as sugarcane and grain (corn and wheat) unexpectedly led to an increase in global food prices and raised ethical problems with converting food to energy. Therefore, technologies for bioethanol production from non-food biomass or lignocellulose, such as wood and agricultural residues, by means of pretreatment–saccharifica-

tion–fermentation are being aggressively studied. However, the energy conversion rates for these materials are low because of the three main components of lignocellulose (cellulose, hemicellulose, and lignin), only cellulose undergoes fermentation. Technologies for fermenting xylan, a type of hemicellulose, are under development but are not yet in practical use. On the contrary, gasification and catalytic liquefaction rapidly convert various kinds of whole biomass to gaseous or liquid fuel with high conversion rates and, consequently, have the potential to become practical, high-efficiency processes.

Gasification technology itself has been developed well thus far. According to the World Gasification Database (2007), existing world gasification capacity was 56,238 MWth of syngas output from 144 operating plants and about 400 total gasifiers [2]. Details of feedstock showed coal was dominant (30,835 MWth, 54.8% in total), then was petroleum 18,454 MWth, 32.8%. Biomass/wastes had very low share of 2.0%. Products of coal gasification were FT liquids and chemicals (49%, 32% respectively), on the other hand, products of biomass/wastes were gaseous fuels and power. It is necessary to develop biomass gasification from now, basing and modifying on coal gasification.

Many types of gasifiers have been studied; the main types include fixed-bed, rotary kiln, fluidized-bed, and entrained-flow gasifiers. Small-scale gasifiers are already in practical use for the generation of electric power and the cogeneration of power and

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heat. Power generation or cogeneration requires gas with a high calorific value, but control of the gaseous components is unnecessary because the gas is combusted. To reduce both initial and operational costs, an air-blown gasifier is usually used, and the gas produced contains 30–50% nitrogen. Gasifiers developed for power generation and cogeneration thus far have been fixed-bed and fluidized-bed types [3,4].

In contrast, for the catalytic synthesis of liquid fuel, both the gaseous components and the impurities must be controlled. Because liquid fuel and other chemical products are usually synthesized from H_2 and CO, the ratio of H_2 to CO has to be controlled to suit the desired products; for example, the ideal $[H_2]/[CO]$ ratio for the synthesis of methanol and Fischer–Tropsch synthesis oil is ~ 2 . Even though N_2 gas is inert, it increases the energy required for compression and decreases the energy efficiency of the gasifier. In addition, the amount of impurities that deactivate the catalyst must be reduced; for example, the sulfur content must be <1 ppm [5,6].

Fluidized-bed and entrained-flow gasifiers are commonly used for liquid fuel synthesis and chemical production. The entrained-flow gasifier has many advantages; for example, it has a simple structure, no catalyst is required, the tar yield is low, control of the gaseous components is easy, and various kinds of biomass are available as feedstock.

As mentioned before, the entrained-flow gasifier was initially developed for gasifying coal, and now for coal gasifiers are operated, such as GE Energy, Shell, and Lurgi, in large scales of a few thousand ton/day in the world. In Japan, two demonstration plants are now in operation; an oxygen-blown, two-stage spiral-flow gasifier is used in an integrated coal gasification fuel cell combined-cycle plant under the Coal Energy Application for Gas Liquid & Electricity (EAGLE) Project, and an air-blown entrained-flow gasifier is used in an integrated coal gasification combined-cycle plant in Nakoso [7–9]. Co-gasification of coal and biomass using an entrained gasifier also has been developed and demonstrated, adopting for the integrated gasification combined-cycle plants. The content of biomass to coal is as low as 3–10 wt.%, so coal gasification is the base in principal, however, modifications are required. There have been few reports on the co-gasification using an entrained-flow gasifier, basic research about co-gasification reactivity of coal and woody biomass is reported [10].

In biomass (alone) gasification using an entrained-flow gasifier-liquid fuel synthesis process, two cases are well known in the world. One is a black liquor gasification-DME synthesis by CHEMREC Co. Ltd., in Sweden [11,12], the other is a two-stage gasification of woody biomass –FT synthesis by CHOREN and Shell Co. Ltd., in Germany [13]. The former is gasification of liquid material and the latter is the two-stage gasification, in which wood is pyrolyzed at lower temperature to produce carbonized solid material at 1st stage, then the carbonized material is gasified at higher temperature in an entrained gasifier at 2nd stage. Both gasification processes have been developed by companies and are now on demonstration and/or partially commercialization stages, and the final target scales planned are very large, as large as a few thousand ton/day scale, almost equal to scale of coal gasification. So collection of feedstock biomass would be one of the most important key factors. In general, amounts of biomass are estimated to about 50–100 ton/day, up to 200 ton/day at most, so gasification process suitable for biomass scale should be developed.

As the composition and characteristics of biomass are quite different from those of coal, the gasifier and the plant would also have to be modified for biomass gasification from the following points. The oxygen and fixed carbon contents of biomass are respectively about 45 wt.% and 20–25 wt.%, whereas those of coal are respectively 2–20 wt.% and 50–85 wt.%. The $[H]/[C]$ ratio for biomass is 1.7–2.1, which is higher than that of coal (0.5–0.85). Therefore, biomass is more degradable compared to coal and the gasification

temperature for biomass is lower than that for coal (1300–1600 °C). In biomass, gasification temperatures are reported at 650–1200 °C with and without catalyst, but we consider better to gasify biomass at temperatures of 700–1000 °C (without catalyst case) from both points of energy balance and cost. Because higher temperature consumes much more energy, especially when using steam as a gasification agent, and equipments durable and suitable at high temperatures above 1000 °C become very expensive. Biomass, not like coal, is not expected to contract a large scale and should be treated in energy- and cost-effective conditions.

As part of the High-Efficiency Bioenergy Conversion Project sponsored by the New Energy and Industrial Technology Development Organization, we have been studying the gasification of biomass in an entrained-flow gasifier and clarifying suitable conditions for synthesizing liquid fuels. On the basis of fundamental research, Mitsubishi Heavy Industries Ltd., (MHI), Chubu Electric Power Corporation, and our group at the National Institute of Advanced Industrial Science and Technology (AIST) developed a test plant operating at 2 ton/day for the study of woody biomass gasification and liquid fuel (methanol) synthesis (Fig. 1) [14,15]. In this system, steam and oxygen were used and biomass was partially oxidized to give heat for gasification. In Japan, another group (Sakai at NIAS: Nagasaki Institute of Applied Science's group) has performed gasification using an entrained type reactor [16]. In their system, steam alone is used as a gasification agent and other gasification agent (such as oxygen) cannot be introduced, and heat is supplied from outside of a gasifier (external heat supply system), therefore, it is impossible to make up in a large scale (maximum scale is about 1 ton/day scale at most). The latter is the system suitable for locally distributed in small-scale system and is different from our system.

Using the relatively large scale plant, we also investigated the possibility of recycling the char and analyzed the gasification kinetics [17,18]. We developed a small-scale entrained-flow gasifier and used it to gasify various kinds of biomass; we found that the gasification characteristics depended on the gasification conditions and the feedstock biomass [19–21].

In the current study, we gasified empty fruit bunch (EFB) biomass, the waste from fresh fruit bunches of the oil palm. In Southeast Asia (Malaysia and Indonesia), the production of oil from palm has increased year by year and amounts of discharged EFB have also increased in large quantities. Now most of the EFB are left, however these are promising candidates for bio-fuel production.



Fig. 1. Entrained-flow gasifier test plant (2 ton/day) at Kawagoe, Japan.

Oil palm is cultivated in plantation in Southeast Asian countries, however, bio-fuel produced from the EFB and transported to Japan and used in Japan is counted to “biomass energy in Japan”, which contributes to CO₂ mitigation and production of substitute fuel in Japan. We gasified EFB and clarified the gasification characteristics, including the by-products. We also performed thermogravimetric (TG) analysis of EFB using a thermobalance that was specially modified for the analysis of feedstock in the presence of O₂, H₂O (steam), or both. We compared the results obtained from TG analysis and gasification.

2. Material and method

2.1. Biomass feedstock

EFB obtained from fresh fruit bunches of oil palm cultivated in Malaysia was used as feedstock. Elemental and ash analyses of the feedstock EFB are listed in Table 1. EFB was pulverized to be smaller than 60 mesh, and small pellets (3 mm-dia and 1–2 mm long) were made from EFB powder by a hand press and these pellets were fed into the gasifier.

2.2. TG analysis

Fig. 2 shows a schematic of the modified TG analyzer, the design and details of which were reported previously [22]. A thermobalance (Rigaku, TG8120 + HUM-1) was modified for the analysis of samples in a He environment in the presence of H₂O, O₂, or both. Wet He gas (passed through a H₂O bubbler) and dry He gas were mixed in the mixing chamber. Flow rates in the chamber were automatically adjusted to control the humidity. We added an extra port to introduce dry O₂ into the mixing chamber. After being mixed, humidity-controlled gas (a mixture of He, H₂O, and O₂) was fed into the main chamber. TG data were measured from room temperature to 1200 °C and temperature rising rate was 20 °C/min. TG data were obtained under four sets of conditions (He alone, He + H₂O, He + O₂, He + H₂O + O₂).

2.3. Gasifier and gasification method

The entrained-flow gasifier was designed and built in our laboratory (Fig. 3). The height of the gasifier is about 100 cm and the diameter is 10 cm. The design and details of the gasifier have already been reported [23].

H₂O alone or a mixture of H₂O and O₂ was used as the gasification agents. On the basis of results from our previous study of the gasification of Japanese cedar wood [19], we selected the following reaction conditions for this study:

$$\begin{aligned} \text{H}_2\text{O.alone}([\text{O}_2]/[\text{C}] = 0, \text{constant}), \\ [\text{H}_2\text{O}]/[\text{C}] = 0.5, 2.5, \text{and } 5.0 \text{ (three conditions)} \end{aligned} \quad (1)$$

$$\begin{aligned} \text{H}_2\text{O} + \text{O}_2([\text{H}_2\text{O}]/[\text{C}] \approx 2.5, \text{constant}), \\ [\text{O}_2]/[\text{C}] = 0, 0.15, \text{and } 0.35 \text{ (three conditions)} \end{aligned} \quad (2)$$

The reactor was heated to 900 °C in a N₂ atmosphere, and then the gasification agent (H₂O or H₂O + O₂) was fed into the reactor from the bottom. The EFB pellets were introduced from an automatic feeder installed at the top of the reactor and were passed through a feedstock conduit to the reactor bottom. During falling down in the conduits and blowing up by gasification agents from the bottom of the gasifier, the pellets were broken into pieces, entrained in the gasifier and gasified. The produced gas was collected after passing through a filter, a cooler, and a drain. Gas volume was measured using a gas meter (Shinagawa Gas meter, DC-1a), and gas composition was analyzed with a gas chromatograph (Shimadzu GC-14A equipped with an MS-5A column for H₂ and CO, a Porapak column for CO₂, and a Squalane column for CH₄ and C₂₊ gases). The fraction consisting of solid material recovered from the filter and from the reactor bottom was defined as “solid residue,” and the fraction obtained by washing the cooler with acetone, distilling off the acetone, and collecting the residue was defined as “tar.” We used the following equation to calculate the gasification index and the yields of solid residue and tar:

Gasification rate

$$= [\text{mol C in evolved gas (CO + CH}_4 + \text{CO}_2 + \text{C}_2+)] / [\text{mol C in biomass feedstock}]$$

Yield of solid residue (wt.%)

$$= 100 \times (\text{weight of solid residue}) / (\text{weight of feedstock biomass})$$

Yield of tar (wt.%)

$$= 100 \times (\text{weight of tar}) / (\text{weight of feedstock biomass})$$

3. Results and discussion

3.1. TG analysis

Fig. 4 shows the TG curves of EFB samples obtained under the four sets of conditions. Under all conditions, the decomposition rate of EFB was highest at temperatures between 260 °C and 340 °C, and the rates in this temperature range were nearly identical for all conditions. However, under He alone, EFB decomposed gradually and linearly between 340 °C and 800 °C, whereas the addition of H₂O or O₂ to the He accelerated the decomposition, which occurred at a lower temperature and was nearly complete at around 600 °C. At around 1000 °C, the residual weights in all four conditions were 2.6–3.0 wt.% to original weights, almost equivalent to ash contents weights. In the TG analysis, it takes about 60 min. from 100 to 1200 °C, and 20 min. from 600 to 1000 °C. Though it takes much longer time than actual residence (gasification) time, these results suggested EFB did not contained “fixed-type” carbon so much and would decompose easier. We compared our results to results obtained for Japanese cedar wood, a typical woody biomass used in Japan (The TG curve for cedar wood has been reported but is not shown here [24,25]). The weight loss for EFB was larger than that for cedar wood at both 260–340 °C and 380 °C: for example, the weight loss percentages were 72.5% for He alone and 72.9% for (He + H₂O + O₂) at 340 °C for EFB, compared to 41% for He alone and 44% for He + H₂O + O₂ for Japanese cedar wood. Japanese cedar wood has high lignin (Klason lignin) content (35%) [20], whereas EFB has a Klason lignin content of ~22% [26]. We have already reported that lignin itself (organo-solve-lignin) and high-lignin-content woody biomass, such as

Table 1
Elemental and ash analyses of EFB feedstock (wt.%).

Elemental analysis	C	H	N	O*	Ash
EFB	46.3	5.9	0.5	44.6	2.7
J. cedar wood***	48.6	6.1	–	45.1	0.36
Elemental analysis of EFB ash	>10 wt.% K (56), Si (12)	**	1–10 wt.% Ca (4.6), Mg (3.5), P, Fe		<1 wt.% S, Al, Cl

(Gasification of Japanese cedar wood itself was not described in this paper, but properties were mentioned comparing to those of EFB I discussion).

* Calculated by subtraction.

** Values wt.% in ash; values in parentheses wt.% for each element in ash.

*** Data is shown as reference.

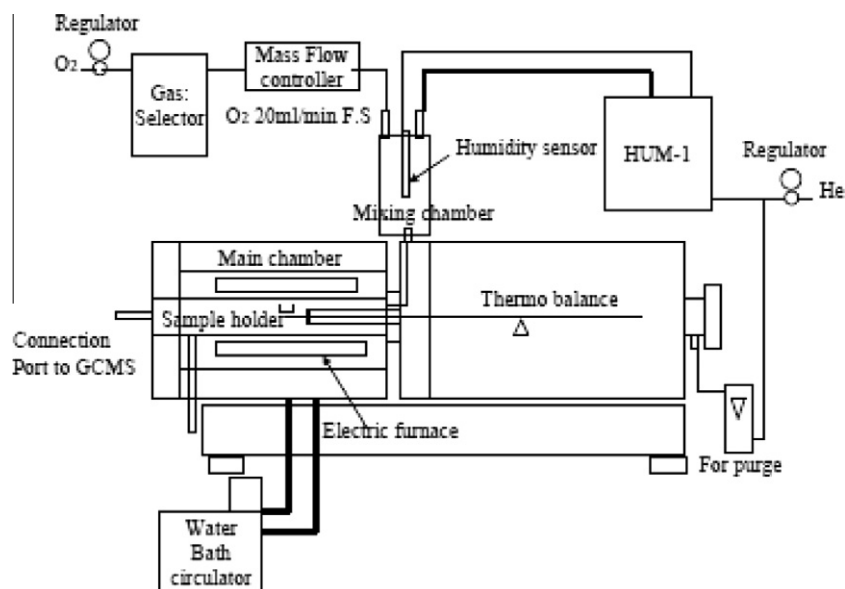


Fig. 2. Schematic of TG analyzer.

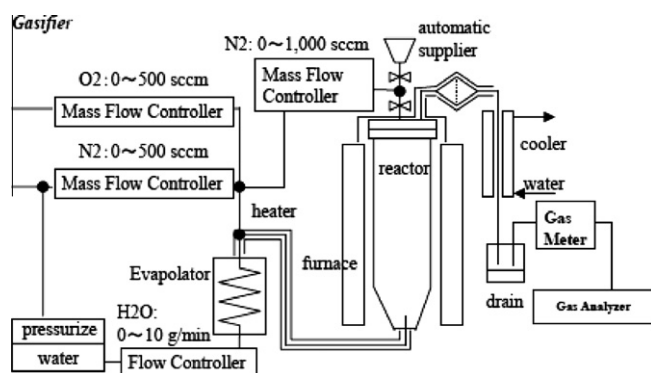


Fig. 3. Schematic of small-scale entrained-flow gasifier.

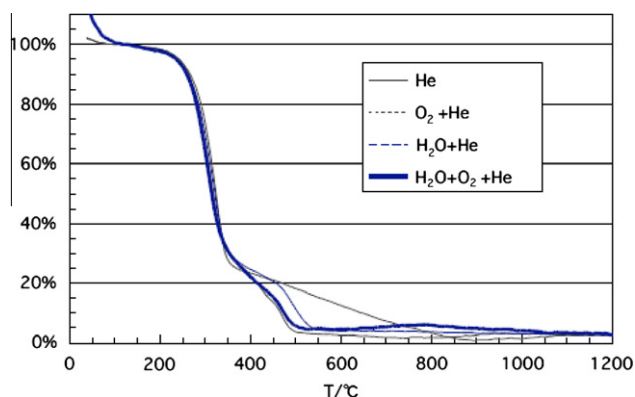


Fig. 4. TG curves for EFB gasification under various conditions.

cedar bark, do not decompose or gasify as well as cedar wood and low-lignin-content woody biomass, such as delignified bark, and that the lignin components increase the difficulty of gasification. Our current results suggest that EFB decomposed at a lower temperature than did cedar wood and that gasification of EFB would proceed more rapidly than that of cedar wood.

3.2. Gasification

3.2.1. Product distribution after gasification

In this experimental series, EFB was gasified under five conditions of different combinations of $[H_2O]/[C]$ ratio and $[O_2]/[C]$ ratio. Gases existing and flowing through the gasifier were seal gas (N_2), gasification agent gases (H_2O and O_2) and produced gases from EFB (CO , CH_4 , CO_2 , H_2 and C_2+ gases). Residence times, which were dependent on volume of the gasifier, amounts of gases flew through the gasifier and changed as time went, were roughly estimated to be 18–61 s, the shortest (18 s) was under the condition of ($[H_2O]/[C] = 5$, no O_2) and the longest (61 s) was under the condition of ($[H_2O]/[C] = 0.5$, no O_2). When $[H_2O]/[C]$ was 2.5 (constant) and $[O_2]/[C]$ was changed (0, 0.15, 0.35), residence times were estimated to be about 26–31 s. In any condition, it did not attain equilibrium condition.

In the presence of H_2O alone (Table 2), at a low $[H_2O]/[C]$ ratio (0.5), though the residence time was long, the gasification rate was not high (86.5 C-equivalent%). We previously reported that when Japanese cedar was gasified under various combinations of $[H_2O]/[C]$ ratio and $[O_2]/[C]$ ratio, with the increase of $[H_2O]/[C]$ ratio (and residence times got shorter), gasification rate also increased, however above the $[H_2O]/[C]$ ratio 5 there was no significant difference in gasification rate [19]. In EFB, the gasification rate was also higher at the higher $[H_2O]/[C]$ ratios, and at a $[H_2O]/[C]$ ratio of about 2.5, EFB was gasified well. The tar yield was low (<0.1 wt.%) under all three conditions. A small amount of solid residue consisting mainly of ash and carbon was obtained.

In the presence of O_2 and H_2O (Table 3), gasification proceeded further than in the presence of H_2O alone, and at a $[O_2]/[C]$ ratio of 0.35, gasification proceeded almost completely (>99.5 C-equiva-

Table 2

Product distribution after gasification of EFB with H_2O alone.

$[H_2O]/[C]$ ratio*	0.5	2	4.2
Gasification rate (C-equivalent%)**	86.9	95.8	90.0
Solid residue yield (wt.%)	3.4	2.8	3.0
Tar yield (wt.%)	<0.1	<0.1	<0.1

* Gasification temperature, 900 °C.

** $[\text{mol C in evolved gas (CO, CO}_2, \text{CH}_4, \text{C}_2+)]/[\text{mol C in feedstock biomass}]$.

Table 3Product distribution after gasification of EFB with H₂O + O₂.

[O ₂]/[C] ratio ^a	0	0.1	0.35
Gasification rate (C-equivalent%) ^{**}	95.8	92.2	100.4
Solid residue yield (wt.%)	2.8	3.2	2.8
Tar yield (wt.%)	<0.1	<0.1	<0.1

^a Gasification conditions: 900 °C, [H₂O]/[C in feedstock biomass] mol ratio ≈ 2.^{**} [mol C in evolved gas (CO, CO₂, CH₄, C₂₊)]/[mol C in feedstock biomass].

lent%), almost all the carbon in the feedstock was converted into gas, and the solid residues consisted almost entirely of ash. Both H₂O and O₂ were very effective to increase gasification rate.

In Tables 2 and 3, yields of solid residues and tar are shown as weight percentages relative to the weight of the original feedstock EFB, and the gas yields are shown as carbon conversion rates (carbon-equivalent yields). Carbon distribution into the products after gasification is a commonly used parameter, but we found that the elemental analysis data for the solid residues obtained after gasification implied a chemical composition that was not reasonable for organic compounds. This issue is discussed in detail in Section 3.2.4.1.

3.2.2. Product gases

CO, CH₄, CO₂, and H₂ were the primary product gases, and C₂₊ gases accounted for <0.5 vol.% (Fig. 5). As above mentioned, the residence times were estimated to be 18–61 s, and these were not in equilibrium state in any experiment, however, gas compositions became steady and almost constant (not equilibrium composition) several minutes after beginning of EFB supply and hereafter.

In the presence of H₂O alone, the percentage of (H₂ + CO) in the total gas evolved was as high as 67–75%. As the [H₂O]/[C] ratio was increased, the amount of CO decreased and the amounts of H₂ and CO₂ increased as the water shift reaction proceeded: at a [H₂O]/[C] ratio of 2.5, the [H₂]/[CO] ratio was about 3.5, which is higher than that for Japanese cedar wood (2–2.5) and other wood. Gas compositions were dependent on properties of biomass feedstock. However, between EFB and Japanese cedar wood there is no significant difference in elemental analysis except ash contents and composition of ash (Table 1). As noted in Table 1, potassium, calcium, and magnesium were present in relatively high amounts in the ash of EFB (potassium made up more than

half the ash); these alkali and alkali earth metals reportedly accelerate gasification, and we also found these metals' effect on gasification from our results of DTF measurements using char obtained through gasification of cedar wood and bark. [18] We attributed both the high gasification rate and the progress of the shift reaction to the high contents of these alkali and alkali earth metals.

In previous studies of the gasification of Japanese cedar wood and other woody biomass, we found that as the amount of O₂ added to the H₂O was increased, the amounts of H₂ and CO decreased: however, the amount of H₂ decreased more than the amount of CO, so the [H₂]/[CO] ratio decreased. We also found that the amount of CO₂ increased as the amount of O₂ added to the H₂O increased. Therefore, the gas compositions were not suitable for liquid fuel synthesis, because a [H₂]/[CO] ratio of 2–2.5 is usually required. In the current study, we also observed that the amounts of both H₂ and CO decreased as the amount of O₂ was increased. However, we obtained a [H₂]/[CO] ratio of 2.7 at an [O₂]/[C] ratio of 0.35, which was high enough for liquid fuel synthesis.

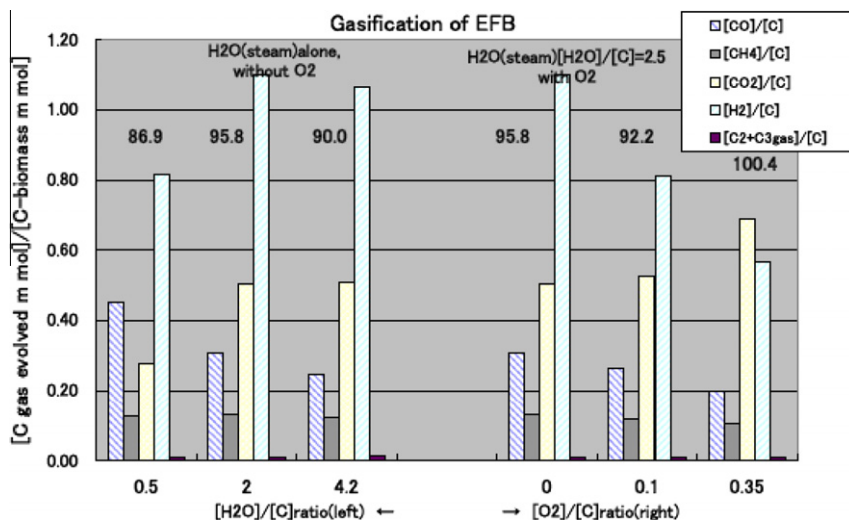
Our gasification results (Tables 2 and 3, Fig. 3) indicate that EFB was gasified well enough in the presence of H₂O alone to produce a product gas enriched in H₂ gas and that the process was suitable for liquid fuel synthesis. Adding O₂ to H₂O further accelerated the gasification, and the [H₂]/[CO] ratio, which was lower than that for H₂O alone, remained high enough for liquid fuel synthesis.

3.2.3. Comparison of the results from TG analysis and gasification

The TG curves showed EFB was almost completely decomposed at around 600 °C in the presence of H₂O or H₂O + O₂ whereas a relative amount remained at 600 °C and gradually decomposed above 600 °C in He alone. It also showed that EFB was decomposed at a lower temperature (~600 °C) than that required for cedar wood in the presence of H₂O. These TG data suggested that EFB would be gasified well using H₂O alone as a gasification agent and that EFB would easily be gasified compared to Japanese cedar wood.

The gasification resulted in that EFB was gasified well (gasification rate: about 95%) when using H₂O alone as a gasification agent and gasification rates were higher than those of cedar wood at the same gasification conditions. The temperature drop observed in the TG analyses when O₂ was added was consistent with the increase in the gasification rate when O₂ was added.

TG analyses and gasification results agreed well.

**Fig. 5.** Amounts and composition of product gases produced by gasification of EFB.

3.2.4. By-products of gasification

One of the key advantages of the entrained-flow gasifier is the low yield of tar and solid residues, which we observed in the gasification of EFB: the yields of tar and solid residues were <0.1 wt.% and 2–3 wt.%, respectively. Nevertheless, even these low yields would require treatment in a commercial-scale (50–100 ton/day) plant because ~100 kg of tar and 2–3 ton of solid residues would be produced every day in such a plant. Characterizing these by-products is the first step toward reducing them.

3.2.4.1. Tar. Tar was recovered from three different zones (cooler, drain, and pipe), and the recovered amount was largest from the cooler. Elemental analysis indicated that the tar consisted of carbon and hydrogen alone (carbon, 94.3%; hydrogen, 6.3%). GC–MS analysis indicated that the compounds in the tar from the three zones were almost the same. Fig. 6 shows the spectrum for the tar obtained from the cooler after gasification with H₂O alone ([H₂O]/[C] = 2 and [O₂]/[C] = 0). Six polycyclic aromatic compounds (naphthalene, acenaphthylene, phenanthrene, anthracene, fluoranthene, and pyrene) made up 90% (peak strength) of the tar, and several other polycyclic aromatic compounds, such as chrysene and benzofluoranthene, were detected at levels <1% (peak strength).

In tar obtained in the presence of H₂O + O₂, the same six polycyclic aromatic compounds were identified, but the naphthalene content was higher than in the tar obtained with H₂O alone, making up nearly 50% of the total tar, and the pyrene and fluoranthene contents were lower (spectrum not shown). In tar derived from biomass gasification, a large number of compounds (over 100 species) have been reported [27]. Our detection of only six compounds in the tar indicates that the primary and secondary tar generated during the first stage were quickly decomposed during gasification and that the tar underwent further degradation in the presence of oxygen.

3.2.4.2. Solid residues. The solid residues obtained after gasification were soft, yellow products that partially adhered to the gasifier wall. Table 4 shows elemental analysis of solid residues obtained under two different sets of gasification conditions (EFB-1 and EFB-2). As mentioned previously (Section 2.1), the elemental analysis of the solid residues gave anomalous results. The oxygen content is generally determined not directly but by difference (100%: original feedstock weight – [sum of weights of carbon, hydrogen, nitrogen, sulfur, and ash]) by means of a method developed mainly for coal analysis (JIS). The original EFB feedstock was analyzed according to this method, and the oxygen content was calculated by difference (Table 1). However, this method gave an “oxygen content” of 19.35 wt.% for EFB-1, which suggested that the residue had a chemical composition of CH_{0.46}O_{5.05} (N < 0.01), which is not reasonable for organic compounds. There-

Table 4

Elemental analysis of solid residues after gasification of EFB under two sets of conditions.

	C	H	N	Ash	Difference
EFB-1	3.83	1.77	0.05	75.01	19.35
EFB-2	1.10	1.60	0	83.57	13.73

Gasification conditions: EFB-1, [H₂O]/[C] = 2, [O₂]/[C] = 0; EFB-2, [H₂O]/[C] = 2, [O₂]/[C] = 0.35.

fore, in Table 4, we use the term “difference” rather than “oxygen content.”

We consider the reasons the anomalous behavior of the solid residue in the elemental analysis is the following. For ash content analysis, the sample was ashed and oxidized to remove carbon, oxygen, hydrogen, and nitrogen; and the residue, which consisted mainly of oxidized metals, was defined as ash. By means of this procedure, salts of alkali and alkali earth metals originally present in a sample in the form of carbonate, hydrogen-carbonate, nitrate, or sulfate were converted to oxidized forms. We have reported that char obtained through gasification of cedar wood contained a relative amounts of CaCO₃ and other alkali and alkaline earth carbonates and that when three kinds of biomass (cedar wood, cedar bark and mixture of hardwood) were ashed at temperatures ranging from 600 to 900 °C, various kinds of metallic compounds remained after ashing at 600 °C but oxidized or recomposed to be more stable at above 800 °C [28]. Although the weight of oxidized metals was lower than the weight of the metals in their original forms, the total weight of oxidized metals was defined as the weight of ash.

When considerable amounts of metals in unoxidized form were contained in solid residues from EFB, weight losses were large, and the difference was considered to be the oxygen content.

In addition, a certain metal, such as potassium, partially vaporized or did not form a stable oxidized product (It is known K₂O is unstable and is easily and rapidly degraded in the air, especially in the presence of water, and we also reported potassium compounds vaporized more ashing temperature rose [28]), therefore, potassium existed in the solid residue was also missing during analyzing process and the “missing” was also counted as “difference”.

Alkali and alkali earth metals in biomass are known to exist mainly as carbonates, phosphates, hydrates, nitrates, and sulfates. Solid residues EFB-1 and EFB-2 were recovered from the gasifier after gasification at 900 °C, at which temperature most of the carbonates, hydrogen-carbonates, and other salts would have been degraded. To clarify the difference of elemental analysis and forms of metals in solid residues, we analyzed the solid residues using Fourier transform infrared spectroscopy (FT-IR) and identified the functional groups present in the residues.

Fig. 7 shows the FT-IR profile of EFB-1 (the profile for EFB-2 was nearly identical). Peaks derived from potassium hydrogen-carbon-

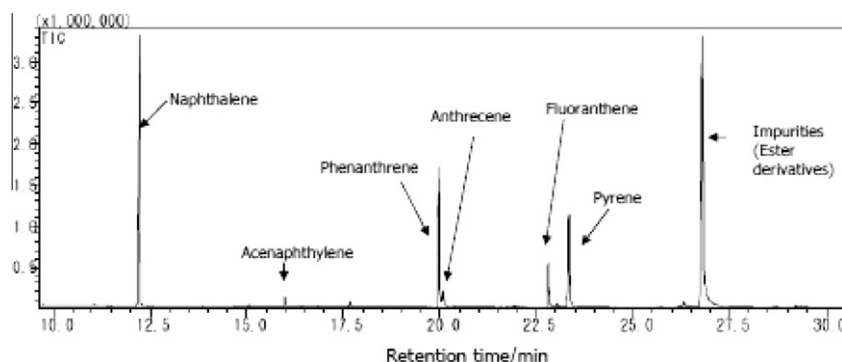


Fig. 6. GC–MS spectrum of EFB-2 residue.

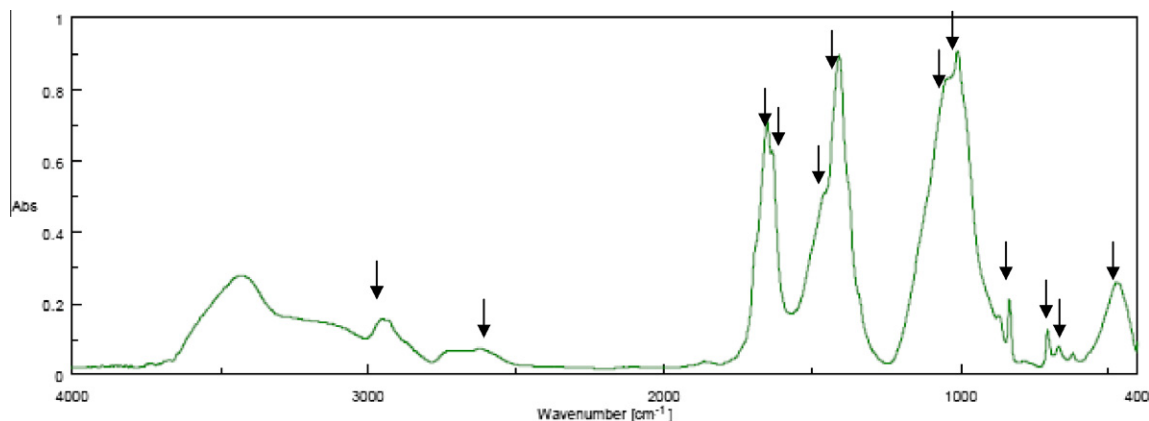


Fig. 7. FT-IR spectrum of EFB-1 solid residue.

Table 5

Correspondence between FT-IR peaks for EFB-1 and reference samples.

EFB-1	2953	2624	1850	1652	1635	1455	1410	1040	1008	868	834	703	667	620	471
KHCO ₃	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
K ₂ CO ₃				○	○	○		○		○		○	○		
CaCO ₃						○				○					
CaSiO ₃													○		○
SiO ₂													○		○

ate, potassium carbonate, calcium carbonate, meta-calcium silicate, and silicate are present. The broad peak at 3300–3500 cm⁻¹ indicating the presence of a hydroxide functional group was attributed to moisture in the sample. The correspondence between the peaks in the EFB-1 sample and the peaks for authentic samples was good (Table 5).

During the cooling of the gasifier after gasification at 900 °C, solid residues were exposed to steam and the product gases (CO, CO₂, CH₄, and H₂). We assume that the metals present on the surface of the solid residue reacted with CO₂, H₂, and steam to form carbonates and other salts (e.g., CaO + CO₂ → CaCO₃). When these carbonates and other forms of alkali and alkali earth metals were oxidized, their weights were reduced (e.g., CaCO₃ → CaO + CO₂). These weight changes were counted as the calculated oxygen content.

4. Conclusion

EFB was gasified well with H₂O (steam) alone as a gasification agent to produce a hydrogen-rich gas suitable for liquid fuel synthesis. The gasification rate increased to >99% when O₂ was added to the H₂O; however, the amount of CO₂ in the product gas increased, the amounts of CO and H₂ decreased, and the [H₂]/[CO] ratio decreased. Nevertheless, the [H₂]/[CO] ratio remained high enough for liquid fuel synthesis. The results obtained from TG analysis and gasification agreed well. The tar collected after gasification consisted mainly of six polycyclic aromatic compounds, and its yield was quite low, which suggests that degradation of the tar proceeded quite well. Although the yield of solid residues was low, the residues partially adhered to the gasifier wall and would have to be treated in a large-scale gasification process.

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